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(21) International Application Number: PCT/US90/05894 (22) International Filing Date: 15 October 1990 (15.10.90) (30) Priority data: <table border="0"> <tr> <td>421,873</td> <td>16 October 1989 (16.10.89)</td> <td>US</td> </tr> <tr> <td>422,164</td> <td>16 October 1989 (16.10.89)</td> <td>US</td> </tr> <tr> <td>436,283</td> <td>13 November 1989 (13.11.89)</td> <td>US</td> </tr> <tr> <td>497,293</td> <td>22 March 1990 (22.03.90)</td> <td>US</td> </tr> <tr> <td>497,294</td> <td>22 March 1990 (22.03.90)</td> <td>US</td> </tr> <tr> <td>497,295</td> <td>22 March 1990 (22.03.90)</td> <td>US</td> </tr> <tr> <td>Not furnished</td> <td>12 October 1990 (12.10.90)</td> <td>US</td> </tr> </table> (71) Applicant: AKZO N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL). (71)(72) Applicants and Inventors: WANG, Bor-Ping, Eric [-/US]; 84 Hudson Point Lane, Ossining, NY 10562 (US). BAND, Elliot, Isaac [US/US]; 19 Pine Street, North Tarrytown, NY 10591 (US). PIOTROWSKI, Andrzej, Mieczysław [PL/US]; 14 Crestview Avenue, Peekskill, NY 10566 (US). AMATA, Richard, James [US/US]; 817 Terrace Place, Peekskill, NY 10566 (US).		421,873	16 October 1989 (16.10.89)	US	422,164	16 October 1989 (16.10.89)	US	436,283	13 November 1989 (13.11.89)	US	497,293	22 March 1990 (22.03.90)	US	497,294	22 March 1990 (22.03.90)	US	497,295	22 March 1990 (22.03.90)	US	Not furnished	12 October 1990 (12.10.90)	US	(74) Agent: FENNELLY, Richard, P.; Akzo America Inc., Livingston Avenue, Dobbs Ferry, NY 10522 (US). (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>
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(54) Title: PROCESS OF MAKING HALIDE/ALKOXY-CONTAINING MAGNESIUM COMPLEX (57) Abstract <p>Hydrocarbon-soluble complexes of magnesium halo-alkoxides and alcohols ($X_nMg(OR)_{2-n}mR'OH$ pR''OH) are prepared in a non-Grignard reaction involving combination of sources of magnesium, halide, and alkoxide in the presence of an excess of the alcohol for the desired alkoxy group and an amount of lower alkyl alcohol to effect the desired solubilization of the complex.</p>																							

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PROCESS OF MAKING HALIDE/ALKOXY-CONTAINING
MAGNESIUM COMPLEX

BACKGROUND OF THE INVENTION

5 Magnesium compositions containing halide and alkoxy
moieties of the general formula $X_nMg(OR)_{2-n}$, where n is in the
range of $0 < n < 2$, are known and have been found to be useful
as olefin polymerization catalyst supports or components (see
U.S. Patent No. 4,209,602).

10 Several recent examples of disclosures relating to this
general area of technology include the following:

U.S. Patent No. 4,727,051 to M. J. Breen et al. describes
such compounds in which the R group of the alkoxy ligands is
 C_1-C_{10} alkyl which are formed by (a) preparing an adduct of a
magnesium halide and an alkanol; (b) reacting the product from
15 step (a) with metallic magnesium; and drying the product of
step (b) at an elevated temperature.

U.S. Patent No. 4,792,640 to V. C. Mehta describes
hydrocarbon-soluble compounds of the formula $ROMgX$, where R is
a primary 2-alkyl substituted radical containing 5 to 18
20 carbon atoms and X is halide. These compounds are formed by
reacting activated magnesium metal with an alkyl halide in an
inert solvent to form a Grignard reagent which is then reacted
with an oxygen-containing compound, including an alcohol, to
produce the desired compound $ROMgX$.

25 U.S. Patent No. 4,820,879 describes preparation of
hydrocarbyloxy magnesium halides by reacting activated
magnesium metal with an oxygen-containing compound and an
anhydrous hydrogen halide.

SUMMARY OF THE INVENTION

30 The present invention, in its broadest sense, involves a
process for forming hydrocarbon-soluble halide, alkoxy-
containing magnesium complexes in a non-Grignard reaction
(i.e., not involving reaction of a dialkylmagnesium compound

and an alkyl halide as essential reactants to form a compound having the formula RMgX where X is halide and R is alkyl). The present process relies upon the combination of appropriate sources of magnesium, halide, and alkoxide in the presence of a slight excess of the parent alcohol for the desired alkoxy group (OR) and an amount of a lower alkyl alcohol (e.g., an alcohol containing an alkyl group of from about one to about four carbon atoms) to effect solubilization of the resulting complex.

The amount of "free" alcohol (combined amount of parent and lower alkyl alcohol) which should be used to achieve solubility needs to be no less than about 6 wt% of the composition. "Free" alcohol is the excess alcohol present as compared to the molar amount of magnesium present in the complex. As the "free" alcohol concentration is decreased below this amount (about 6 wt%), the complex formed tends to become insoluble.

The present invention, in one embodiment, relates to a process for forming a hydrocarbon-soluble complex of a magnesium haloalkoxide and an alcohol by combining a magnesium halide, a magnesium alkoxide and the aforesaid alcohol mixture, in an inert hydrocarbon solvent, to form the hydrocarbon-soluble complex. The combination may be made by first combining the magnesium halide and alcohol followed by addition of the alkoxide. Alternatively, and preferably, the alkoxide and magnesium halide are first combined followed by addition of the mixture of alcohols.

The present invention, in another embodiment of the invention, relates a process of preparing hydrocarbon-soluble complexes of a magnesium haloalkoxide and an alcohol by combining a magnesium halide with hydrocarbon solvent or solvents and alcohols followed by heating, if necessary, to dissolve the halide and form a solution, followed by addition of a magnesium metal source. The term "magnesium halide" is inclusive of compounds of the formula MgX_2 where X is halogen, e.g., chlorine. The term "alcohol" is inclusive of compounds of the formula ROH where R is a C_1 to C_{12} straight or branched

alkyl group, e.g., 2-ethylhexyl or an aralkyl group, e.g., benzyl alcohol. The term "hydrocarbon solvent" is inclusive of such solvents as toluene, alkyl alcohols such as ethanol, or mixtures thereof, which can be used to enhance the
5 solubility of the magnesium halide.

The present invention, in accordance with yet another embodiment of the invention, relates a process of preparing hydrocarbon-soluble complexes of a magnesium haloalkoxide and an alcohol by forming a mixture of magnesium metal in
10 hydrocarbon solvent, adding magnesium halide thereto, followed by addition of the alcohols.

DETAILED DESCRIPTION OF THE INVENTION

The present invention, in its broadest sense, involves a process for forming hydrocarbon-soluble halide, alkoxy-
15 containing magnesium complexes in a non-Grignard reaction (i.e., not involving reaction of a dialkylmagnesium compound and an alkyl halide as essential reactants). The present process relies upon the combination of appropriate sources of magnesium, halide, and alkoxide in the presence of a slight
20 excess of the parent alcohol for the desired alkoxy group (R) and an amount of a lower alkyl alcohol (e.g., an alcohol containing an alkyl group of from about one to about four carbon atoms) to effect solubilization of the resulting complex.

One embodiment of the process of the instant invention comprises the initial step of dissolving a magnesium halide (such as magnesium dichloride) in an alcoholic solvent (such as a branched 2-alkyl substituted alcohol containing 5 to 12 carbon atoms as exemplified by 2-ethyl-1-hexanol) followed by
30 heating (e.g., to about 100° C). To the resulting reaction mixture is then added a magnesium C₁-C₄ alkoxide, such as magnesium ethoxide and an organic solvent, such as heptane. The reaction medium is then heated and any added solvent is thereby removed. Another process embodiment which is
35 preferred involves the initial combining of magnesium halide

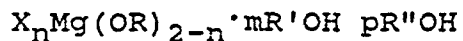
and magnesium alkoxide, in an appropriate solvent, followed by addition of the alcohol. This procedure will result in less alcohol being needed than the first procedure since in the first process embodiment the magnesium halide will tend to form an initial adduct with the alcohol thereby using more of that additive than in the second process embodiment.

The first step of yet another embodiment of the general process of the instant invention comprises the formation of a solution by the admixture of magnesium halide, hydrocarbon solvent or solvents, and alcohol. This admixture can be brought about by first combining the solvent(s) (e.g., toluene and ethanol) and alcohol to form a solution to which the magnesium halide is added followed by appropriate heating to effect dissolution of the magnesium halide. It has been found that ethanol, for example, if mixed with the alcohol first to form a solution can increase the solubility of the magnesium halide in forming the solution to which the magnesium metal source is added. This step yields a solution. The second step involves the addition of a magnesium metal source (either magnesium metal itself or a dialkylmagnesium compound) to form the desired reaction product which is further described below. This particular embodiment of the general process described herein is economically more attractive than processes which utilize relatively more expensive magnesium alkoxide reagents in such synthesis procedures. It also has the advantage of achieving a soluble system initially with its combination of magnesium halide, solvent(s), and alcohols thereby making it easier to achieve a final soluble product after the magnesium metal source is added.

The first step of yet another embodiment of the general process of the instant invention comprises the formation of a mixture of magnesium in an appropriate hydrocarbon solvent, e.g., heptane, and heating the solution. Preferably, the magnesium metal can be suitably activated. One preferred way is to also add a magnesium dialkyl (e.g., butyl ethyl magnesium) to the solvent containing the magnesium metal. To

the resulting reaction mixture is then added a magnesium halide, preferably magnesium chloride. This addition is then followed by addition of alcohol, preferably a mixture of a C₁-C₄ alkyl alcohol, such as ethanol, and a branched (e.g., 2-alkyl substituted) C₅-C₁₂ alcohol, such as 2-ethylhexanol. Heat is applied to achieve the desired production of the reaction product described below. In this embodiment, the relatively expensive magnesium alkoxide reagent has been replaced with magnesium metal and appropriate parent alcohol.

The resulting reaction product from any of the previously described embodiments of the general procedure first described above, which is soluble in hydrocarbon solvents, such as heptane, is a complex of a magnesium haloalkoxide and an alcohols. It may be represented by the formula



where X is halogen, R, R' and R'' are hydrocarbyl radicals (such as C₁-C₁₂ alkyl) and can be the same or different, n is in the range of 0 < n < 2, and m+p is in the range of 0 < m+p < 4. Preferably, R' can be C₁ to C₄ alkyl and R'' can be C₅-C₁₂ branched alkyl.

The instant invention is further understood by the Examples which follow.

EXAMPLE 1

Magnesium chloride (48.5 grams) was suspended in 210 grams of 2-ethyl-1-hexanol, and the suspension was heated to 100° C. At this point, 57 grams of magnesium ethoxide was
5 added followed by 300 ml of heptane. The reaction mixture was stirred vigorously and was sparged with nitrogen to remove solvent. After 150 ml of solvent was evaporated, fresh heptane was added, and the reaction mixture was sparged with nitrogen until almost all solvent was removed. The reaction
10 mixture temperature was 99° C at the beginning of the evaporation and 130° C at the end. The product, in the form of a very viscous oil, was dissolved in 500 grams of heptane and was left overnight to settle. The final product was filtered and diluted with heptane. The solution was analyzed with the
15 following results: Mg wt% 2.70; Cl wt% 3.75; ethanol wt% 4.7; and free 2-ethyl-1-hexanol wt% 9.3.

EXAMPLE 2

The solution from Example 1 was diluted with heptane to contain 1.82% Mg. This solution (100 grams) was then used to prepare 11.7 grams of supported catalyst.

5 The catalyst was prepared from a solution of chloro-magnesium alkoxide containing 1.82% Mg, 2.54% Cl, 6.31% 2-ethyl hexanol, and 3.19% ethanol. One hundred grams of solution containing 75 mmol Mg was added dropwise with stirring to 200 ml of TiCl_4 at -25°C . The mixture was
10 maintained at -25°C for 35 min and was then allowed to warm to room temperature. The mixture was heated to 111°C , at which time, 5.0 grams of diisobutylphthalate was added, and the heating was continued for two hours. The solid was filtered hot, was reslurried in 275 ml of TiCl_4 , was heated for two
15 hours, and was then filtered hot. The solids were washed twice with hot decane, were washed with hexane, and were dried with nitrogen to recover 11.7 grams of powdered catalyst.

The catalyst was tested in combination with triethyl aluminum and an external donor in hexane slurry to polymerize
20 propylene. Hydrogen was added to control the MFI. The polymerization conditions were maintained at 100 psig and 70°C for two hours. The yield was 9070 grams polymer/grams catalyst, with a total isotactic index of 94.4%, a melt flow index of 4.9 grams/10 min., and a tapped bulk density of 0.30
25 gram/ml.

EXAMPLE 3

This Example illustrates the preparation of a hydrocarbon-soluble chloromagnesiumalkoxide in accordance with the present invention. The preparation was conducted under a nitrogen atmosphere. The toluene, ethanol, and benzyl alcohol were dried over molecular sieve resin. Magnesium chloride (22.3 grams, 0.234 mole, under 0.2% water content) was weighed and charged into a 500 ml round bottom flask equipped with stir bar coated with TEFLON fluoropolymer. The vessel was purged with nitrogen. A solution of pure toluene (84 grams), benzyl alcohol (70 grams, 0.647 mole), and absolute ethanol (24.46 grams, 0.532 mole) was then added to the vessel. The vessel was heated to about 100° C for about 20 minutes with stirring until the $MgCl_2$ became dissolved. Magnesium metal turnings (5.65 grams, 0.232 mole) were added to a separate three-neck flask equipped with a mechanical stirrer, dropping funnel, gas inlet, outlet, and solids addition port. Toluene (reagent grade, 43.7 grams) was then added followed by 1.0 gram of butyl ethyl magnesium (10.5% in heptane, 0.022 grams Mg, 9.1×10^{-4} mole). The vessel was heated to about 105° C for 15 minutes with stirring, and was then cooled. The toluene solution which contains $MgCl_2$ /benzyl alcohol/ethanol was transferred into a dropping funnel through a tube of TEFLON fluoropolymer and then was added dropwise into the vessel with stirring. The vessel's temperature was maintained at about 90° C for the addition of the remaining solution. After the addition, the vessel was heated to reflux (about 105° C) and was maintained at that temperature with stirring for one hour. The vessel was cooled, and the liquid was slowly filtered through a 0.5 micron filter. The filtrate was a colorless mobile solution.

The filtrate was mixed with 140.3 grams of toluene to prepare a final solution of 20% $ClMgOC_7H_7$ in toluene/ethanol/benzyl alcohol. The final theoretical composition of the solution was:

ClMgOC ₇ H ₇	78 grams
"Free" benzyl alcohol	19.5 grams
"Free" ethanol	24.5 grams
Toluene	268 grams

Total	390 grams
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Estimated "Free Alcohol": 11.28% wt.

EXAMPLE 4

A 500 ml three-neck flask was equipped with a mechanical stirrer, condenser, gas inlet, outlet and solids addition port. The vessel was purged with nitrogen for 30 minutes replacing the atmosphere with nitrogen.

To this flask was added 103 grams of toluene through a syringe. Under stirring, 59.8 grams (0.553 mole) of benzyl alcohol and 22.2 grams (0.482 mole) of ethanol were charged into the flask. The solution was heated to 80° C. Magnesium chloride (22.3 grams, 0.234 mole) was added slowly through the solids addition port. After the addition was complete, the flask was heated to about 100° C. for 15 minutes until the $MgCl_2$ became dissolved, was then cooled to 75° C, and magnesium metal was added rapidly through the solids addition port under slow nitrogen flow. After the addition, the vessel was heated to reflux temperature and was maintained at that temperature with stirring for two hours. The filtration step was the same as in Example 1. The final theoretical composition of this solution was:

$ClMgOC_7H_7$	78 grams
"Free" benzyl alcohol	9.3 grams
"Free" ethanol	22.2 grams
Toluene	280.5 grams

Total	390 grams
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Estimated "Free Alcohol": 8.08% wt.

EXAMPLE 5

A toluene/ethanol/MgCl₂/benzyl alcohol solution was prepared in accordance with the procedure of Example 2 except less ethanol and benzyl alcohol was used. 57.2 grams of benzyl alcohol and 17.8 grams of ethanol were added. The final theoretical composition of this solution was:

ClMgOC ₇ H ₇	78 grams
"Free" benzyl alcohol	6.7 grams
"Free" ethanol	17.8 grams
Toluene	287.5 grams
<hr/>	
Total	390 grams

Estimated "Free Alcohol": 6.28% wt.

COMPARATIVE EXAMPLE 6

Magnesium chloride, 1.11 grams (0.012 mole) was transferred into a 150 ml vial in a dry box. Substantially pure, dry toluene (40 ml) was then added followed by 5.82 ml (0.056 mole) of benzyl alcohol with stirring. The vial was heated to refluxing temperature for about 5 minutes. At this point, 12.3 grams of butylethylmagnesium (10.5 wt % in heptane, 0.011 mole Mg) was added dropwise to the vial with stirring. After the addition, the vial was maintained at a refluxing temperature for about 5 minutes. The final product was a white solid. This Example illustrates that a solid product was obtained when ethanol was not used in the preparation even if excess benzyl alcohol was present.

COMPARATIVE EXAMPLE 7

Following the procedure of Comparative Example 4, 1.12 grams of MgCl_2 (0.011 mole) was placed in a 150 ml vial along with 40 ml of toluene. Then, 4.5 ml of ethanol (3.53 grams, 0.077 mole) was added to the vial with stirring. The vial was heated to refluxing temperature for about 5 minutes. Then, 8.1 grams of butylethylmagnesium (15.6 wt % in heptane, 0.011 mole Mg) was added dropwise to the vial. After the addition, the vial was maintained at a refluxing temperature for about 5 minutes. The final product, chloromagnesium ethoxide, was a white solid.

COMPARATIVE EXAMPLE 8

In a 150 ml vial, 40 ml of dry toluene was charged by syringe followed by 2 ml of ethanol (1.57 grams, 0.034 mole). Then, 8.0 grams of butylethylmagnesium (15.6 wt % in heptane, 0.011 mole Mg) was added dropwise to the vial. During the addition, gas evolution was observed. After the addition, the vial was maintained at refluxing temperature for about 5 minutes. The final product, magnesium ethoxide, was a white solid.

EXAMPLE 9

Magnesium chloride, 1.11 grams (0.012 mole) of MgCl_2 was transferred into a 150 ml vial in a dry box. Substantially pure dry toluene (20 ml) was then charged by syringe. Under stirring, 3.47 grams (0.032 mole) of benzyl alcohol and 1.1 grams (0.024 mole) of ethanol were added to the vial. The vial was heated to a refluxing temperature for about 5 minutes. Then, 12.2 grams of butylethylmagnesium (10.5 wt % in heptane, 0.011 mole Mg) was added dropwise to the vial with stirring. After the addition, the vial was maintained at a refluxing temperature for about 5 minutes. The final product was a colorless solution. This Example illustrates that a solvent mixture of toluene and heptane allows for production of the desired soluble product.

COMPARATIVE EXAMPLE 10

Magnesium metal (0.28 gram 0.012 mole) and 1.13 gram (0.011 mole) of magnesium metal were placed in a 150 ml vial. Dry toluene (60 ml) was charged into the vial by syringe without ethanol being present as well. Then 6.65 gram of benzyl alcohol (0.06 mole) was added into the vial with stirring. After addition the vial was maintained at refluxing temperature for about 30 minutes. The final product was a white solid.

EXAMPLE 11

This Example illustrates the preparation of another hydrocarbon-soluble chloromagnesium hydrocarbyloxyde. The preparation was conducted under a nitrogen atmosphere. The toluene, ethanol, and (for this Example) 2-octanol were dried over molecular sieves and degassed by purging with nitrogen. Magnesium chloride (22.3 grams, 0.234 mole, under 0.2% water content), toluene (104 grams), 2-octanol (76.7 grams, 0.673 mole), and absolute ethanol (30.4 grams, 0.661 mole) were mixed in a three neck round bottom flask equipment with a mechanical stirrer, condenser, and solids addition port. The vessel was heated to 111° C for about 15-20 minutes with stirring until the $MgCl_2$ dissolved. Then, magnesium metal turnings (5.65 grams, 0.232 mole) were added to the solution mixture slowly, with control of the gas and heat evolution. As the reaction subsided, the solution was heated to reflux for 2-3 hours. The solution was then diluted with toluene (about 74 grams) and filtered through a 0.5 micron fluoropolymer (TEFLON brand) membrane in-line filter. Additional toluene (about 200 grams) was added to prepare a 17 wt % off-yellow 2-octoxy chloromagnesium solution.

	Magnesium, metal	5.65 grams	0.233 mole
	Magnesium chloride	22.3 grams	0.234 mole
	Toluene	378 grams	
25	Abs. ethanol	30.4 grams	0.661 mole
	2-octanol	7.4 grams	0.673 mole

	"ClMg(OC ₈ H ₁₇)"	88.3 grams	0.467 mole
	Free "ethanol"	30.4 grams	0.661 mole
30	Free "2-octanol"	23.5 grams	0.206 mole
	Toluene (total)	378 grams	

	Total	520 grams	(17.0 wt % sol'n).

EXAMPLE 12

This Example illustrates the preparation of another hydrocarbon-soluble chloromagnesium alkoxide. The preparation was conducted under a nitrogen atmosphere. The toluene, ethanol, and (for this Example) 2-octanol were dried over molecular sieves and degassed by purging with nitrogen. Magnesium chloride (22.3 grams, 0.234 mole, under 0.2% water content), toluene (104 grams), 2-octanol (76.7 grams, 0.673 mole), and absolute ethanol (30.4 grams, 0.661 mole) were mixed in a three neck round bottom flask equipped with a mechanical stirrer, condenser, and solids addition port. The vessel was heated to 111° C for about 15-20 minutes with stirring until the $MgCl_2$ dissolved. Then, magnesium metal turnings (5.65 grams, 0.232 mole) were added to the solution mixture slowly, with control of the gas and heat evolution. As the reaction subsided, the solution was heated to reflux for 2-3 hours. The solution was then diluted with toluene (about 74 grams) and filtered through a 0.5 micron fluoropolymer (TEFLON brand) membrane in-line filter. Additional toluene (about 200 grams) was added to prepare a 17 wt % off-yellow 2-octoxy chloromagnesium solution.

	Magnesium, metal	5.65 grams	0.233 mole
	Magnesium chloride	22.3 grams	0.234 mole
	Toluene	378 grams	
25	Abs. ethanol	30.4 grams	0.661 mole
	2-octanol	7.4 grams	0.673 mole

	"ClMg(OC ₈ H ₁₇)"	88.3 grams	0.467 mole
	Free "ethanol"	30.4 grams	0.661 mole
30	Free "2-octanol"	23.5 grams	0.206 mole
	Toluene (total)	378 grams	

	Total	520 grams (17.0 wt % sol'n)	

EXAMPLE 13

This Example illustrates the preparation of magnesium chloroalkoxide. The process was conducted under a nitrogen atmosphere. The ethanol and 2-ethylhexanol used were dried over molecular sieve resin. Magnesium metal turnings (5.40 grams, 0.222 mole) of over 98% purity were added to a 500 ml flask equipped with a mechanical stirrer, dropping funnel, gas inlet, outlet, and solids addition port. The vessel was purged with nitrogen. Heptane (pure grade, 40 grams) was then added followed by 12.0 grams of butyl ethyl magnesium (10% in heptane, 0.264 grams Mg, 0.011 mole Mg, 10.7 grams heptane). The vessel was heated to about 100° C for about 15 minutes with stirring, and was then cooled. Magnesium chloride (22.3 grams, 0.234 mole, under 0.2% water content) was then added rapidly through the solids addition port under a slow nitrogen flow, minimizing any possible exposure to air. A solution of pure heptane (60 grams), 2-ethylhexanol (83.4 grams, 0.642 mole), and absolute ethanol (22.0 grams, 0.478 mole) were added dropwise to the vessel with stirring over 15 minutes. During the initial addition, the vessel heated up to about 55° C, and viscosity increased. Subsequently, it began to cool and viscosity decreased with the addition of more alcohol. At this point, the vessel was heated to 80° C and was maintained at this temperature for the addition of the remaining solution. It was important to insure that there was vigorous H₂ gas evolution throughout the addition to prevent the possibility of a sudden pressure surge in the vessel. After the addition, the vessel was heated to reflux (about 103° C) and was maintained at that temperature with stirring for two hours. The vessel was cooled and the liquid was slowly filtered through a 40-60 micron frit. Depending on the frit, there may be some slight cloudiness to the filtrate which slowly settles and may be removed by careful decantation with a diptube.

The filtrate was mixed with 195 grams heptane without precipitation of any solids to prepare a final solution of 20

wt% Cl-Mg-OC₈H₁₇ in heptane/ethanol/2-ethylhexanol. The final theoretical composition of this composition was:

	ClMgOC ₈ H ₁₇	88 grams
	"Free" 2-ethylhexanol	23 grams
5	"Free" ethanol	22 grams
	Heptane	<u>306</u> grams
	Total	439 grams

COMPARATIVE EXAMPLE 14

10 Magnesium chloride, 1.11 grams (0.012 mole) MgCl₂ was transferred into a 150 ml vial in a dry box. Forty ml of pure dry toluene was then charged by syringe. Under stirring, 6.0 grams (0.056 mole) of benzyl alcohol was added by syringe. The vial was heated to refluxing temperature for about 5 minutes. At this point, 12.3 grams of BEM (10.5 wt% in
15 heptane, 0.011 mole Mg) was added dropwise into the vial. After the addition was completed, the vial was maintained at refluxing temperature for at least 5 more minutes. The final product was a white solid. This Example showed that the solid product was obtained when large excess of reactant alcohol has
20 been used.

The foregoing Examples are represented by certain embodiments of the invention and should not therefore be construed in a limiting sense. The scope of protection sought is set forth in the claims which follow.

We Claim:

- 5 1. A process for forming hydrocarbon-soluble halide, alkoxy-containing magnesium complexes in a non-Grignard reaction which comprises the combination of sources of magnesium, halide, and alkoxide in the presence of an excess of the parent alcohol for the desired alkoxy group and an amount of a lower alkyl alcohol to effect solubilization of the resulting complex.
- 10 2. A process as claimed in Claim 1 which comprises combining a magnesium halide, a magnesium alkoxide, and an alcohol in an inert hydrocarbon solvent to form the complex.
- 15 3. A process as claimed in Claim 2 which comprises initially combining the magnesium alkoxide and magnesium halide in the inert hydrocarbon solvent followed by addition of the alcohol thereto.
- 20 4. A process as claimed in Claim 2 which comprises dissolving the magnesium halide in alcohol and thereafter adding the magnesium alkoxide and solvent thereto.
5. A process as claimed in Claim 2 wherein the magnesium halide is magnesium dichloride.
6. A process as claimed in Claim 2 wherein the magnesium alkoxide is a magnesium C₁-C₄ alkoxide.
7. A process as claimed in Claim 5 wherein the magnesium alkoxide is a magnesium C₁-C₄ alkoxide.
- 25 8. A process as claimed in Claim 2 wherein the magnesium halide is magnesium dichloride and the alcohol is a mixture of alcohols.

9. A process as claimed in Claim 1 wherein the alcohols comprise a mixture of a C₁ to C₄ alkyl alcohol and a C₅ to C₁₂ branched alkyl alcohol.

5 10. A process as claimed in Claim 2 wherein the magnesium halide is magnesium chloride, the magnesium alkoxide is a magnesium C₁-C₄ alkoxide, and the alcohol is a C₅ to C₁₂ branched alkyl alcohol.

10 11. A process as claimed in Claim 10 wherein the alcohol is 2-ethyl-1-hexanol and the magnesium alkoxide is magnesium ethoxide.

12. A process as claimed in Claim 1 which comprises combining magnesium halide with a solution comprising the alcohols and solvent and forming a solution therefrom and by thereafter adding a magnesium metal source to the solution.

15 13. A process as claimed in Claim 12 wherein the magnesium metal source is selected from the group consisting of magnesium metal and a dialkylmagnesium compound.

14. A process as claimed in Claim 12 wherein the magnesium halide is magnesium chloride.

20 15. A process as claimed in Claim 12 wherein the magnesium halide is magnesium chloride and the alcohol which is added comprises an alkyl group or an aralkyl group.

25 16. A process as claimed in Claim 12 wherein the solvent comprises ethanol and the magnesium halide is magnesium chloride.

17. A process as claimed in Claim 1 wherein the magnesium halide is magnesium chloride and the alcohol comprises an aralkyl group.

18. A process as claimed in Claim 17 wherein the alcohol is benzyl alcohol.

19. A hydrocarbon solution containing dissolved therein a complex of a magnesium halohydrocarbyloxyde formed
5 by the process of Claim 1.

20. A process as claimed in Claim 1 which comprises forming a mixture of magnesium metal and another hydrocarbon solvent, adding magnesium halide thereto, and then adding the alcohols.

10 21. A process as claimed in Claim 20 wherein the mixture of magnesium metal and hydrocarbon solvent additionally comprises a dialkyl magnesium activating agent for the magnesium metal.

15 22. A process as claimed in Claim 20 wherein the magnesium halide is magnesium chloride.

23. A process as claimed in Claim 20 wherein the magnesium halide is magnesium chloride and the alcohols which are added comprise a 2-alkyl substituted branched alcohol having 5 to 12 carbon atoms.

20 24. A process as claimed in Claim 20 wherein the alcohol also comprises ethanol and the magnesium halide is magnesium chloride.

25 25. A process as claimed in Claim 20 wherein the magnesium halide is magnesium chloride and the alcohol comprises a mixture of a C₁-C₄ alkyl alcohol and a C₅-C₁₂ branched alkyl alcohol.

26. A process as claimed in Claim 25 wherein the alcohol comprises a mixture of ethanol and 2-ethylhexanol.

27. A process as claimed in Claim 25 wherein the mixture of magnesium metal and hydrocarbon solvent additionally comprises a dialkyl magnesium activating agent for the magnesium metal.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/05894

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC U.S. 502/111; 502/125; 502/171 IPC 5 B01J 31/00 ; 37/00																							
II. FIELDS SEARCHED <div style="text-align: center; margin-top: 5px;">Minimum Documentation Searched ⁷</div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 30%; padding: 5px;">Classification System</th> <th style="padding: 5px;">Classification Symbols</th> </tr> <tr> <td style="padding: 5px; text-align: center;">U.S.</td> <td style="padding: 5px;">502/111; 502/125 ; 502/171</td> </tr> </table> <div style="text-align: center; margin-top: 5px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	U.S.	502/111; 502/125 ; 502/171																	
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; padding: 5px;">Category [*]</th> <th style="width: 70%; padding: 5px;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%; padding: 5px;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X Y</td> <td style="padding: 5px;">US, A, 4,806,696 (Job) 21 February 1989. See column, lines 35-47 and the paragraph bridging columns 1 and 2.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1,2,5-7,19 3,4,8-12</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;">US, A, 4,792,640 (Mehta) 20 December 1988;</td> <td style="text-align: center; vertical-align: top; padding: 5px;">8,-11,15,17,</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;">US, A, 4,727, 051 (Breen et al) 23 February 1988; See the examples.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">12-18,20-27</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 4,335,016 (Dombro) 15 June 1982;</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-27</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 4,105,585 (Mateson) 8 August 1978;</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-17</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 3,859,231 (Kochhar) 7 January 1975. See the entire document.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-27</td> </tr> </table>			Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X Y	US, A, 4,806,696 (Job) 21 February 1989. See column, lines 35-47 and the paragraph bridging columns 1 and 2.	1,2,5-7,19 3,4,8-12	Y	US, A, 4,792,640 (Mehta) 20 December 1988;	8,-11,15,17,	Y	US, A, 4,727, 051 (Breen et al) 23 February 1988; See the examples.	12-18,20-27	A	US, A, 4,335,016 (Dombro) 15 June 1982;	1-27	A	US, A, 4,105,585 (Mateson) 8 August 1978;	1-17	A	US, A, 3,859,231 (Kochhar) 7 January 1975. See the entire document.	1-27
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>																							
IV. CERTIFICATION <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;"> Date of the Actual Completion of the International Search 17 DECEMBER 1990 </td> <td style="width: 50%; padding: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em; font-weight: bold;">11 FEB 1991</div> </td> </tr> <tr> <td style="padding: 5px;"> International Searching Authority ISA/US </td> <td style="padding: 5px;"> Signature of Authorized Officer <i>Nguyen Ngoc Ho</i> <div style="display: flex; justify-content: space-between;"> E. D. IRZINSKI NGUYEN NGOC-HO </div> <div style="text-align: right; font-weight: bold;">INTERNATIONAL DIVISION</div> </td> </tr> </table>			Date of the Actual Completion of the International Search 17 DECEMBER 1990	Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em; font-weight: bold;">11 FEB 1991</div>	International Searching Authority ISA/US	Signature of Authorized Officer <i>Nguyen Ngoc Ho</i> <div style="display: flex; justify-content: space-between;"> E. D. IRZINSKI NGUYEN NGOC-HO </div> <div style="text-align: right; font-weight: bold;">INTERNATIONAL DIVISION</div>																	
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